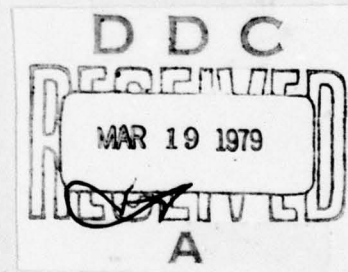# FOREIGN TECHNOLOGY DIVISION

CERTAIN PRINCIPLES OF LONG-WAVE SEMICONDUCTOR PHOTOGRAPHY

By

L. G. Paritskiy and S. M. Rybkin

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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CERTAIN PRINCIPLES OF LONG-WAVE SEMICONDUCTOR PHOTOGRAPHY

L. G. Paritskiy and S. M. Rybkin

Photographing in infrared (IR) rays is an urgent, but far from solved, problem in the contemporary science and technology. The direct photographic methods based on the use of sensitizing dyes, and also the indirect methods with the use of the electron-optical converters, make it possible to obtain photographic images of approximately 1.3 μ, which constitutes only an insignificant part of the entire range of the IR spectrum. The methods based on the heat activity of IR radiation (evaporography, etc.) have a low sensitivity and, apparently, cannot represent basis for obtaining the same photographic characteristics which are inherent in a contemporary silver halide photograph. The scanning converters used at the present time for IR images realize a television element-by-element principle of reading and processing of information which is substantially different from the photographic principle.

This article presents certain general concepts relative to the ways used to create the semiconductor photographic processes, which ensure a fundamental possibility of obtaining photographic images in the broad long-wave region of the spectrum.

1. Effect of Thermal Radiation

The primary and most common reason, which limits the progress of the sensitivity of the silver halide emulsions sensitized to the IR rays into the long-wave region of the spectrum, is the fogging

effect of background thermal radiation.

Actually, immediately after its preparation and throughout the storage and the basic stages of the photographic process, the plate is subjected to the effect of the background IR radiation, which causes fogging of the plate, determines its short life, and prevents the realization of any degree of sensitive photographic process. Even though the qualitative side of thermal radiation is relatively clear, the quantitative calculations of the permissible storage time for the photographic material sensitive to IR rays is of primary significance in estimating the role played by this factor. Czerny was the first one to make such calculations [1] who, proceeding from the impossibility, connected with fogging, of the ordinary photographic methods to make a significant progress into the long-wave range, proposed the evaporography principle.

Using the calculation method which, in its main features, is similar to that in [1], we obtained the curves, shown in Fig. 1, of the photoplate's lifetime t_0 as a function of the long-wave limit of its sensitivity λ_{rp} stored at room temperature (300°K). The different curves depicted in the figure pertain to the varied photosensitivity of the photographic material, expressed in cm^2/erg.

We can see from the figure that, for example, for a photoplate possessing the sensitivity of 1 cm^2/erg up to the limiting wavelength at 1.3 μ, the lifetime at room temperature is approximately two months. When the spectral region of sensitivity is widened to 1.5 μ it drops to one 24-h period, with λ_{rp} at 2 μ - to one minute; and with λ_{rp} at 3 μ it is only tenths of a second. If we accept the lifetime of only one hour at room temperature to be acceptable for practice as the lower limit, then it turns out that the photographic process with a sensitivity at 1 cm^2/erg can be advanced into the IR region to no further than 1.7 μ. Even at the cost of decreasing the sensitivity by 100 times, one can hope to achieve a limiting wave length of only 2.1 μ.

Since the calculation data presented have a totally general nature and are not connected with any specific physical mechanism of formation of a photographic image, it is possible to assume that, still remaining within the framework of traditional methods, IR

photography cannot be extended fundamentally into the long-wave range by more than 2 μ and still retain a certain degree of acceptable photosensitivity.

The results of this calculation, in particular, attest to the fact that seeking new sensitizers which have a greater long-wave sensitivity limit as compared with the existing would be actually useless, because in order to advance the photography further into the infrared region, in any case, one would first have to overcome the long-wave barrier, i. e., the fundamental difficulty connected with the fogging effect of background radiation.

In order to ensure a substantial progress in photography into the IR region of the spectrum without loosing the sensitivity, a certain general principle can be proposed which we will examine below. This principle is presented in section 2 of this article. And, in sections 3 and 4 we give the preliminary results of its specific realization in photographic systems with the use of semiconducting materials.

2. Sensitivity Control Principle

A new quality must be imparted to the photographic process in order to radically reduce the fogging effect of backgrpund radiation - a controlled variability in sensitivity. Let's imagine a photographic process in which the photoplate, after its preparation and during its entire storage period, is insensitive to illumination. However, during the exposure when an effective distribution of illumination is projected onto the plate, a certain controlling factor is activated, which communicates the sensitivity to the photographic material and which terminates its activity at the end of exposure. Thus, its sensitivity is again deactivated for the entire storage period of the exposed plate, its development, and subsequent processing.

The photographic process in which one could activate the sensitivity only for the time of exposure would be free of deficiencies inherent in the present-day IR photography since the time, during which the fogging of the photographic material occurs under the effect of background thermal radiation, is reduced to the limits of the time interval of activity of the effective light signal,

which makes it possible to ensure virtually limitless periods of storage for the plate before and after the exposure.

At the present time a number of processes and devices can be proposed for a practical realization of the controlled sensitivity. Below we will consider the description of the experimentally realized versions of such photographic processes for the IR region of the spectrum with the use of semiconductive materials. In one such process, photosensitivity is controlled by bringing into a mechanical contact of two, initiallly separate, parts of a photographing system during the exposure, each of which does not have a photographic sensitivity individually but this sensitivity appears after the contact that was mentioned is established. We will refer to these processes as the contact-sensitization semiconductive photographic processes.

In the second type of processes, photosensitivity was controlled by the application of an electrical field to the photorecording system or by closing the electrical circuit; in this case, photographic sensitivity appears only at the moment when the field is active or when the electrical current is passing. Subsequently, we will refer to these processes as the electrically controlled semiconductive photographic processes.

3. Contact-Sensitizing Semiconducting Photographic Processes

In the process realized experimentally the photorecording system consisted of a thin layer of a semiconducting photosensitive material which was brought into contact with an aqueous solution of an electrolyte. Naturally, the illumination of the semiconducting layer does not lead to the formation of a photographic image. The electrolyte solution, in itself, is not sensitive to light. However, after the semiconductor is brought in contact with the solution at the interface, oxidation-reduction reactions can occur whose special feature is in the dependence of their rate on the concentration of electrons (holes) in the semiconductor, i. e., on the illumination intensity of the semiconductor.

The reactions which depend on the concentration of the carriers can, as is known [2, 3], lead to three basic changes on the semiconductor's surface: to the precipitation of the metal atoms oxidized

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from the solution, to the dissolution of the semiconducting material (pickling), and, finally, to the formation of the oxide layer. The occurrence of these processes at a different rate on the illuminated and unilluminated areas of the semiconductor layer leads to the formation of a visible or latent photographic image* on the surface of the semiconductor. At the completion of the exposure the reactions on the semiconductor's surface can be terminated by eliminating the contact between the solution and the semiconductor (or by some other means) so that after the exposure the semiconductor plate is again insensitive to illumination.

Thus, to obtain photographic images in the IR region of the spectrum, in principle, we can employ a broad class of the oxidation-reduction reactions on the surface of the semiconductor brought in contact with the electrolyte. In this case the device used to photograph should ensure the realization of a long-wave sensitivity of the semiconductor material and the realization of a controlled sensitivity.

Figure 2 shows a mock-up of a photographic camera which photographs in the manner described.

Semiconductor photoplate 1 attached to the sliding frame 2 is pressed agains the swing-in camera 3. A working electrolyte solution fills the camera from container 4 with elastic walls for the period of exposure. Objective 5 projects an optical image onto the surface of the semiconductor plate. After the completion of exposure the working solution is transferred from the camera back to container 4.

Figure 3 show examples of images obtained by this method on certain semiconducting materials. Fig. 3, a shows an image of a standard television test obtained on a plate made of silicon 100 μ thick. A solution of $CuSO_4$ with the addition of hydrofluoric acid

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* We note that the oxidation-reduction processes with the consideration of the nonequilibrium carriers are used rather extensively and are studied intensively (for example, [4]) in the semiconductor technology. However, in this work, we analyze the possibility of using the reactions of this type for the advancement of photographic methods in the IR region based on the principle of the controlled photographic sensitivity.

was used as the electrolyte. The photographing was done through an IR light filter, IKS-3. The exposure time before the appearance of a visible image was 1—2 s with the illumination of approximately 10^{-4} W/cm^2.

The plates used permit one the use of a "physical" development in the developers of usual composition, which makes it possible to hope for a considerable increase in photosensitivity.

The resolution is 20 lines/mm.

Fig. 3, b shows an example of a picture taken through a germanium light filter (the transmission region is from 1.8 μ) on a semiconductor photoplate made of a semitransparent layer of sulfurous lead sprayed onto glass. A solution of $AgNO_3$ served as the electrolyte.

During the photographing process the plate could have been exposed until a visible image appeared or the exposure could have been interrupted in the stage of latent image with subsequent magnification of the optical blackening density by "physical" development, and also by proping with gold.

The plate sensitivity depends on the technology of their manufacture. For most samples the exposure period, when exposed through a germanium light filter, was 1 min with the illumination at 10^{-4} W/cm^2. The resolution exceeds 20 lines/mm. It is possible to obtain the lined and half-tone pictures. As in the previous example, the image is negative formed by the precipitation of the metal layer on the surface of the semiconductor. Fig. 3, c shows an example of a relief image obtained by photoetching. We used a very thin semiconductor plate of gallium arsenide of the n-type in contact with the electrolyte solution containing HNO_3. In this case the image formed due to selective etching of the semiconductor surface.

The possibility of obtaining photographic images as a result of the oxidation-reduction reactions on the surface was established also for some other semiconductors (lead selenide, indium arsenide).

Electrically controlled semiconducting photographic processes

The general feature of these processes is the presence of a unique "electrical shutter", which permits the "activation" of the photosensitivity for the period of exposure. Just as in other

systems with controlled sensitivity, in this case, generally speaking, there is no need to use complex mechanical and other types of shutters which ensure the interruption of the luminous flux.

Two types of electrically controlled photographic processes were realized experimentally - liquid and a photographic process with the use of an independent current-sensitive film. Fig. 4 depicts the liquid electrically controlled process.

Semiconductive layer 1 equipped with a conducting transparent coating 2 is brought into contact with the electrolyte solution 3, which has a metallic counter-electrode 4. After the projection of an optical image onto layer 1 from the outside, an electric voltage from source 5 is applied to the electrodes 2 and 4. Due to the difference in the rates of an electrolytic precipitation of the metal from the electrolyte solution on the illuminated and unilluminated areas of the semiconducting layer, a latent photographic image is formed on its surface which can then be intensified in the physical developer.

The nature of the processes leading to the formation of latent image can be simply explained by the energy scheme shown in Fig. 5. With an appropriate selection of the electrolyte composition, which comes in contact with the semiconductor, the oxidation-reduction processes do not occur with the circuit open even on the illuminated areas of the semiconductor. With the activation of an external voltage, change occurs in the surface bend of the zones and the nonequilibrium minority carriers (electrons) generated by light in the semiconductor get the chance to reach the electrolyte and reduce the metal ions to neutral atoms whose precipitation on the semiconductor's surface forms a photographic image.

Photographing by this method was accomplished with the aid of the camera already mentioned (see Fig. 2), which was equipped with a metallic counter-electrode. The photographing was done onto the plates made from silicon, germanium, and also from lead sulfide deposited onto a conducting transparent layer of SnO_2. The samples that were obtained had approximately the same photographic sensitivity and resolution as those in the contact-sensitizing process. In the case of germanium the resolution turned out to be somewhat

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lower.

It should be noted that in these experiments we were not attemting to obtain high photographic characteristics specifically but were merely trying to establish the possibility of obtaining photographic images in the IR rays. Simple estimates show that the photographic sensitivity and resolution of these methods can be improved considerably.

Another form of realization of the electrically controlled photographic process in IR rays are the devices in which the photographic image is formed not on the semiconductor's surface but on an independent electrosensitive film. In the development of these processes, certain methods of conductography were employed which were proposed in the twenties and thirties for the visible region of the spectrum [5, 6].

A basic diagram of a device used for the IR photography is shown in Fig. 6. Semiconductor layer 1 has a protective coating 3 which has an anisotropic conductivity and represents a compound based on epoxy resin with a conducting inclusion. The ratio of conductivity in the transverse and longitudinal directions reached 10^8. Pressed agains the anisotropic coating is an electrically sensitive film 4 consisting of a gelatin layer on a base which is permeable for liquid, saturated with an electrolyte solution. The consistency of the film surface is such that it permits a very close and reliable adherence along the entire surface. On the other side the electrically sensitive film is coated by counter-electrode 5 in a form of a thin metal foil. The semiconducting photosensitive layer is prepared in the form of a surface-barrier p-n-junction of large area with a high ohmic external region. From the side of illumination the semiconductor layer has an ohmic contact 2. With the application of an external voltage the junction activates in a blocking direction and operates at a load in the form of an electrolytic cell 3—4—5 in a photodiode mode. Under these conditions the current in the circuit is determined by the intensity of illumination. The image forms in the current-sensitive film 4 during the electrolysis.

The advantage of this device is in the fact that the photo-

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sensitive element can be used many times, since after the exposure the electrically sensitive film is separated from the anisotropic layer, developed in a physical developer, washed, and then rolled onto a glass backing and is dried.

When surface-barrier p-n-junction on silicon was used as the photosensitive layer and the photographing was accomplished through the light filter IKS-3, the exposure time for the light intensity of 10^{-4} W/cm^2 was 5 to 20 s.

With an appropriate selection of the electrolyte composition and the electrode materials, the operation is possible without the application of an external voltage. In this case the "electric shutter" is realized by a simple closing of the circuit.

Simple calculations show that, taking into account the sensitivity level achieved of the p-n-junctions and photoconductors and also the level of the "intensification coefficient" during physical development, photographic sensitivity approaching the average level of sensitivity of negative materials for the visible region of the spectrum can be achieved in the processes described above, which realize the principle of controlled sensitivity for the photography in the IR rays.

In all phases of this work the authors enjoyed an unfailing support and aid from the late vice president of the AS USSR, academician Boris Pavlovich Konstantinov, at whose initiative the studies on the use of semiconductors in photography began.

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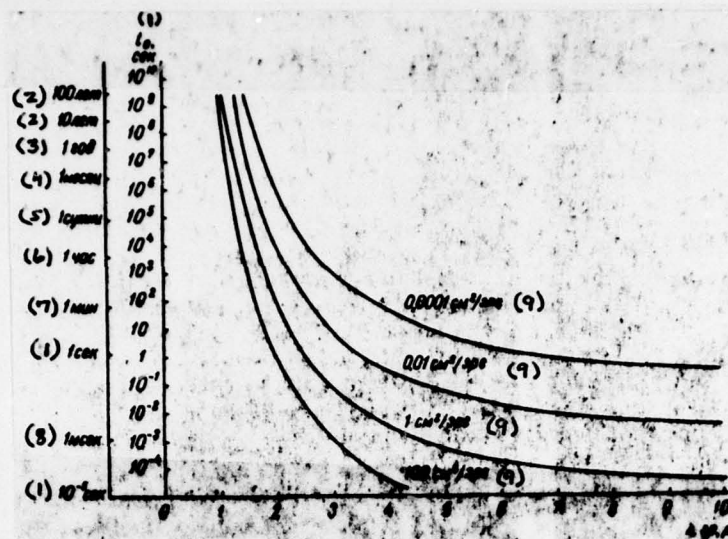
Fig. 1. Fogging time of a photoplate due to background thermal radiation at room temperature as function of the long-wave limit of its sensitivity ($\lambda_{\text{гр}}$).

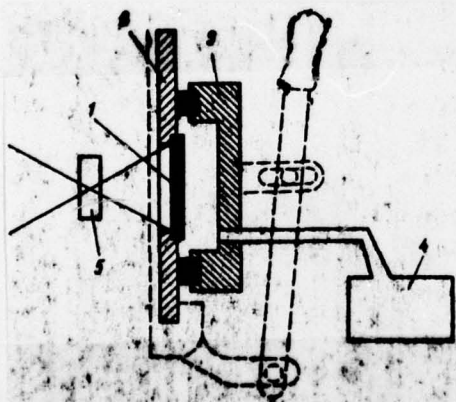KEY: (1) s (2) yrs (3) yr (4) mo (5) 24 h (6) h (7) min (8) ms (9) erg

Fig. 2. A diagram of a photographic camera for photographing in a contact-sensitizing liquid process: 1 - semiconductor plate; 2 - frame; 3 - swing-in camera; 4 - container with an electrolyte; 5 -objective
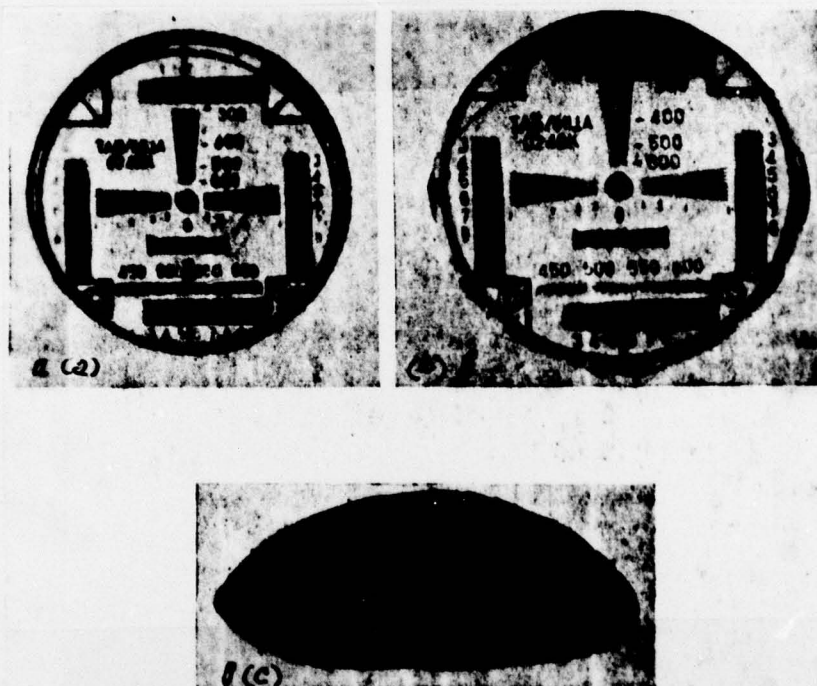
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Fig. 3. Examples of photographs obtained by the contact-sensitizing method: a - on a silicon plate; b - on a plate consisting of a lead sulfide layer (magnified 4 times); c - on a gallium arsenide plate.
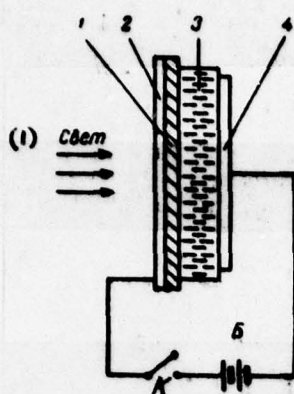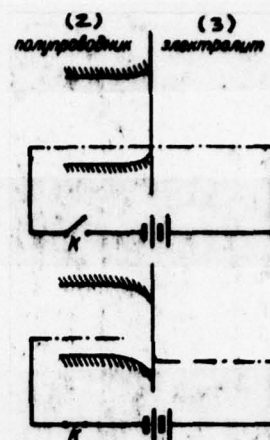
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Fig. 4.

Fig. 5.

Fig. 4. A diagram of a device for an electrically controlled liquid process: 1 - semiconducting layer; 2 - transparent conducting coating; 3 - electrolyte; 4 - counter-electrode

Fig. 5. Energy diagram of electrolysis controlled by light on a semiconducting electrode.

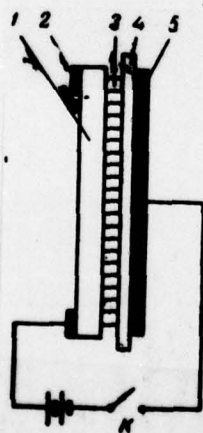KEY: (1) Light (2) Semiconductor (3) Electrolyte

Fig. 6. A diagram of a device for the electrically controlled process with an independent current-sensitive film: 1 - semiconducting plate with a surface-barrier p-n-junction; 2 - ohmic contact; 3 - protective layer with anisotropic condcutivity; 4 - current-sensitive film; 5 - counter-electrode.

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